
Corrosion-Resistant Non-Carbon Electrocatalyst Supports for Proton Exchange Fuel Cells

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- Nissan Technical Center, North America, Farmington Hills, MI
- University of New Mexico, Albuquerque, NM

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Overall Objectives

- Design, develop, and demonstrate high-surface-area (>70 m²/g), high-conductivity (>0.2 S/cm) and corrosion-resistant (as per funding opportunity announcement requirements) non-carbon supports based on doped/mixed metal oxides (that do not contain platinum group metals).
- Derivatize said supports to yield functional supported platinum (Pt) electrocatalysts that leverage strong metal-support interactions (SMSI).
- Demonstrate stability, activity, and performance approaching the DOE 2020 targets, using DOE-prescribed accelerated protocols in rotating disk electrode (RDE) and membrane electrode assembly (MEA) proton exchange fuel cell (PEFC) experiments, by optimizing the structure of the support and the structure of the electrode.
- Provide DOE with at least six 50-cm² MEAs prepared using the best down-selected formulations that (a) meet all the stability

metrics, and (b) provide a clear pathway to meeting DOE 2020 targets for Pt loading and mass activity metrics.

Fiscal Year (FY) 2018 Objectives

- Density functional theory (DFT) calculations to evaluate conductivity and Pt-SMSI of relevant doped metal oxides (MOs).
- Synthesis and characterization of niobium (Nb)-doped-TiO₂ (NTO) and antimony (Sb)-doped-SnO₂ (ATO).
- Characterization of the doped metal oxides and the derived Pt catalysts.
- Electrochemical evaluation of the stability of supports and Pt/MO electrocatalysts.
- Investigation of SMSI in Pt/doped-MO systems using X-ray photoelectron spectroscopy (XPS) and DFT
- Measurement of beginning-of-life (BoL) oxygen reduction reaction (ORR) activity and electrochemically active surface area (ECSA) of selected catalysts in RDE experiments.
- Electrode optimization: RDE and MEA.
- Evaluation of selected catalysts in a PEFC: BoL ORR activity, ECSA, and fuel cell performance.

Technical Barriers

Fuel cell catalyst and catalyst support durability, catalyst performance, and catalyst cost need to be improved, in line with DOE 2020 targets from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.¹

Technical Targets

Table 1 shows the current status (with commercial Pt/C and with the Pt/RTO [ruthenium dioxide-titanium dioxide] catalyst developed in our previous DOE Fuel Cell Technologies Office

¹ <https://energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

project) and the proposed targets for the current project. The preliminary data obtained with our proposed approach (see Table 1—Pt/TiO₂-Ta) was obtained without any optimization of the support, the catalyst deposition process, or the electrode preparation process. Clearly, there is much room for improvement in performance and baseline mass activity, which is precisely our goal in this project. These improvements, in conjunction with the enhancement in durability, will allow us to advance toward the DOE 2020 targets. The advantages of our approach over the incumbent technology and any alternate approach (and to even our prior success with RTO) are that we eliminate the noble metal in the support (cost reduction), we ensure 100% tolerance toward start-stop cycling, and we promote SMSI between the support and Pt, providing a pathway to enhance BoL mass activity and stability under load cycling conditions. Hence, the proposed approach addresses the remaining challenges/technical issues and provides a pathway to advance the state of the art and meet the DOE 2020 targets.

FY 2018 Accomplishments

- DFT was used to study the electronic structure of platinum supported on rutile TiO₂ surface doped with Ta and Nb. Decreased overpotential for ORR was predicted on Pt supported on Ta and Nb-doped TiO₂ surfaces relative to unsupported Pt.
- Nb-doped-TiO₂ was synthesized by aerogel method that exhibited a unique combination of high surface area (140 m²/g), high electrical

conductivity (0.3 S/cm), and high porosity. This catalyst retained 78% of its initial ECSA against the 57.6% retained by Pt/C following DOE/Fuel Cell Commercialization Conference of Japan protocol accelerated stability tests and displayed 21% higher ORR mass activity (at 0.9 V vs. reversible hydrogen electrode [RHE]) compared to commercial Pt/C. This marked improvement resulted from engineered SMSIs, which were confirmed by XPS and RDE measurement.

- ATO was synthesized and characterized at Washington University in St. Louis using a xerogel method and Pt-seeded aerogel method. Colloidal Pt deposition method was used to synthesize the catalyst with small Pt particle size. For both catalysts, no obvious decrease in the ECSA was observed during start/stop cycling tests performed in an RDE. In the fuel cell test, after 1,000 and 5,000 cycles, the iV performance for xerogel or aerogel ATO-supported catalyst was indistinguishable from the BoL iV performance (80°C, 90% relative humidity, 200 kPa_{abs}). However, the aerogel ATO-supported catalyst had much better performance than the xerogel ATO-supported catalyst did.

Table 1. Technical Targets

Metric	Units	SoA (Pt/C)	SoA (Pt/RTO)	Approach Status (Pt/Pt-aerogel-ATO)	End Target	DOE 2020 Target
Total PGM content	g/kW	0.55	0.55	0.25	0.25	<0.125
Total PGM loading	mg/cm ²	0.4	0.4	0.2	0.25	<0.125
Voltage at 1.5 A/cm ² (air)	mV	0.45	0.48	0.49	0.55	N/A
Loss in mass activity	% loss	32	33	<10%	<5%	<40
Voltage loss at 0.8 A/cm ²	mV	81	9	<5	<10	30
Voltage loss at 1.5 A/cm ²	mV	182 ⁺	20	24	<20	30
Mass activity @ 900 mV _{IR-free}	A/mg _{PGM}	0.07	0.07	ca. 0.057	0.3	0.44

SoA – state of the art

PGM – platinum group metal

INTRODUCTION

Carbon black is the commonly used catalyst support for PEFC electrocatalysts due to its high surface area and high conductivity. However, under certain automotive fuel cell operation conditions (start-stop), carbon can corrode rapidly [1], resulting in significant and irrecoverable loss in performance. To address this issue, it is desirable to explore non-carbon supports with high conductivity, high surface area, and high corrosion resistance under fuel cell operating conditions. In this project, we will design, develop, and evaluate electrochemically stable, high-surface-area, MO and doped-MO supports and supported Pt electrocatalysts therein. The Pt/MO catalysts should meet the DOE 2020 targets for stability and approach DOE 2020 targets for the BoL mass activity and Pt loading (as per DOE testing protocols).

APPROACH

DFT simulations will be performed to understand the electronic structure of the oxide upon doping and to examine SMSIs between Pt clusters and the support. The DFT results will guide dopant choice and doping levels. Once suitable combinations are identified and evaluated, we will employ the sacrificial support method pioneered by the University of New Mexico, as well as other methods suitable for the purpose, to prepare the supports with high surface area.

The evaluation of the electrochemical stability will be performed following the start-stop DOE protocol, by sweeping (linear ramp) the working electrode potential from 1 to 1.5 V (vs. RHE). The experiment will be performed for 10,000 cycles (at 500 mV/s). Cyclic voltammograms will be recorded at periodic intervals (at a scan rate of 20 mV/s) to investigate any changes in the pseudo-capacitance or the appearance of any new oxidation or reduction peaks (sign of changes in the oxide surface). The Pt catalysts (Pt deposited onto the MO) will be evaluated by using the start-stop and the load-cycling stability protocols. During the load-cycling protocol the electrode containing the Pt/MO catalyst will be cycled between 0.6 and 0.95 V (vs. RHE) for 10,000 cycles employing a square wave. Cyclic voltammograms will be performed periodically to estimate the ECSA. Linear polarization experiments will be performed to estimate mass- and area-specific activities.

RESULTS

DFT with PBEsol+ U method (Hubbard term $U=5$ set for Ti) was used to study the electronic structure of Pt supported on β -Ti₃O₅(001) and β -Ti₃O₅(010) surfaces. Calculations of the interaction energy between Pt(111) and (001) and (010) surfaces of the Magneli phase showed that there is a weaker but favorable interaction between the catalyst and the β -Ti₃O₅(001) support due to the mismatch of the cell parameters of Pt(111) surface and β -Ti₃O₅(001). Namely, the energy of interaction between Pt and β -Ti₃O₅(001) was calculated as -0.03 eV per atom. Based on the optimized structures, DFT predicts that due to the mismatch in the cell symmetry/lattice parameters between Pt(111) and β -Ti₃O₅(001), grain boundaries are expected to exist in Pt that grows on β -Ti₃O₅(001) surface. In the case of the β -Ti₃O₅(010) support, a strong interaction between the Pt(111) and the support was calculated (-0.07 eV per atom), similar to the value calculated between Pt(111) and doped rutile TiO₂ surfaces. We further calculated density of d -states of Pt(111) supported on β -Ti₃O₅(001) or β -Ti₃O₅(010) surfaces to predict the interaction energies between ORR intermediates and Pt supported on Magneli phase surfaces. The results (Figure 1, left) show that depositing Pt on either β -Ti₃O₅(001) or β -Ti₃O₅(010) surfaces lowers the d -band center of platinum by altering its electronic structure, and Pt on Magneli phase titanium oxide is expected to bind oxygen more weakly than supportless Pt does. Thus, *decreased overpotential for ORR is expected on Pt supported on Magneli phase relative to supportless Pt* (Figure 1, right). Based on DFT calculations, the ORR overpotential potential is expected to follow this relation: Pt on Ta/Nb:TiO₂(110) < Ta/Nb:TiO₂(100) \approx Pt on β -Ti₃O₅(001) < Pt on β -Ti₃O₅(010) < Pt.

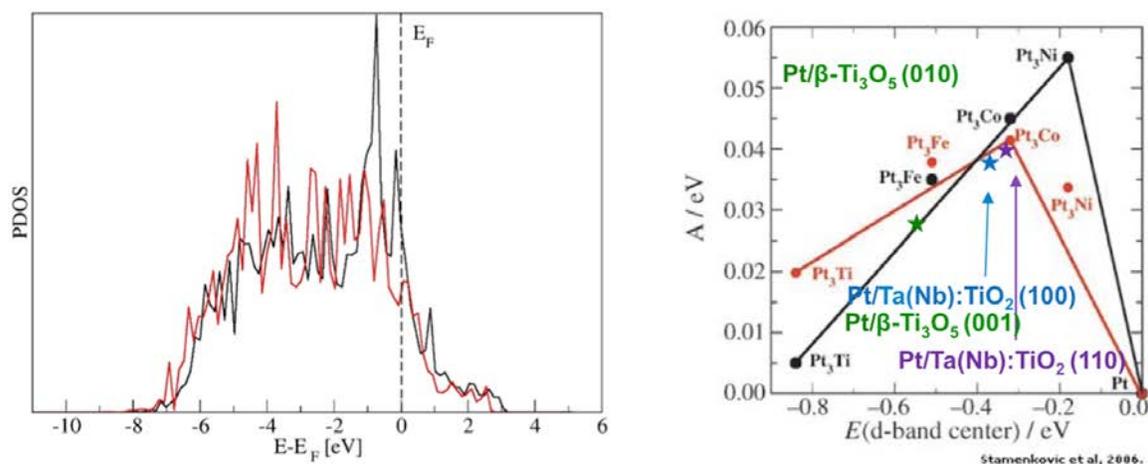
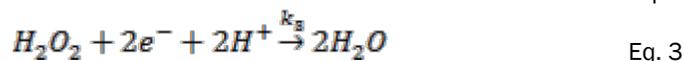


Figure 1. Left: DFT calculated d -projected density of states of Pt(111) supported on β -Ti₃O₅(001) (black) and β -Ti₃O₅(010) (red). Right: Correlation of d -band center for various bulk alloys with the ORR activity (taken from [2]) and comparison with d -band center of Pt supported on TiO₂(110) and TiO₂(100) surfaces doped with 4% Ta and Nb.

Nb_{0.3}Ti_{0.7}O₂ was synthesized by the aerogel method and obtained with high surface area and high conductivity. Pt was deposited on NTO by the formic acid reduction method. The mass activity and half-wave potential of Pt/NTO showed significant improvement compared to commercial Pt/C, suggesting a 20% improvement induced by SMSI. Based on the XPS data, the peak of the Pt 4f for Pt/NTO exhibited a 625 meV shift toward lower binding energy (Figure 2a), suggesting SMSI. Using the RDE technique, the different reaction rate constants for the oxygen reduction reaction (Equations 1–3) were obtained. The result (Figure 2b) shows that in contrast to the carbon support, NTO can significantly increase the reaction rate constant (k_1) via the four-electron-transfer pathway. This can be ascribed to the SMSI between the support and the Pt cluster. The Pt cluster can secure electron donation from the NTO leading to higher electron density around the Pt atom and a decrease in the Pt d-band vacancy. The changes in the electronic structure of Pt/NTO facilitate the transition of adsorbed OH to water by modification of the binding energy of the oxygen-containing species. From Figure 2b, it is also shown that the k_2 of the Pt/C was higher than that of the Pt/NTO. This is because very weak oxygen binding energies impede O–O bond cleavage, while very strong binding energies inhibit the formation of O–H bonds and instead facilitate H₂O₂ formation. The electron structure change of the Pt/NTO should have an intermediate oxygen binding energy.



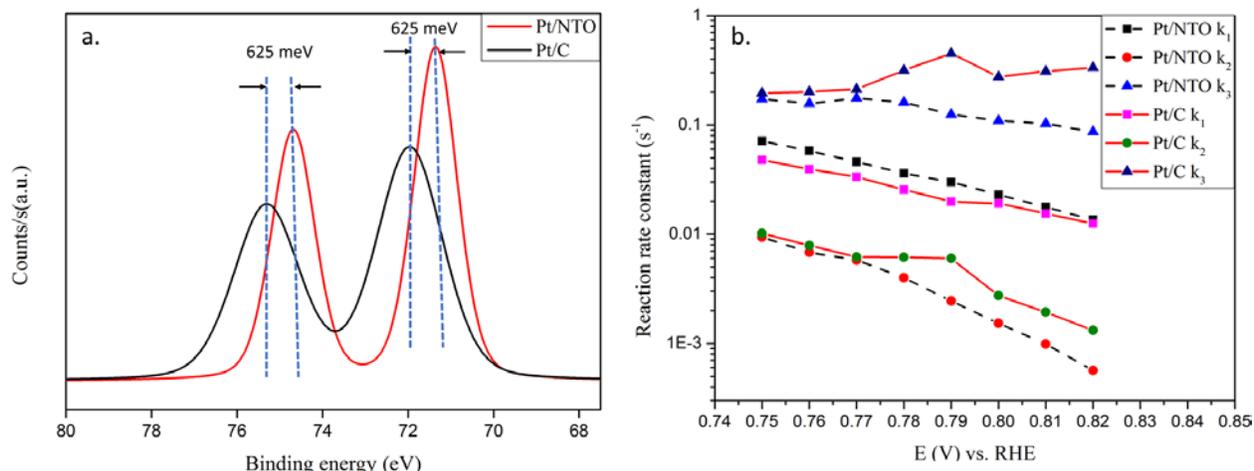


Figure 2. (a) XPS of Pt 4f region of Pt/C and Pt/NTO. (b) The rate constants k_1 k_2 k_3 as a function of potential.

In parallel, $Sb_{0.05}Sn_{0.95}O_2$ (ATO, Sb-doped-SnO₂) was synthesized by the xerogel and Pt-seeded aerogel methods. The Colloidal Pt deposition method was used to deposit Pt on the support. Both catalysts showed good electrochemical stability in RDE under start-stop cycling protocol with less than 10% of ECSA loss after 10,000 cycles (start-stop potential cycles). For the fuel cell test, Pt/Pt-aerogel-ATO displayed similar iV performance with commercial catalyst (Pt on Vulcan carbon); however, Pt/xerogel-ATO displayed poor fuel cell performance (Figure 3). After 1,000 and 5,000 cycles the iV performance for Pt/Pt-aerogel-ATO and Pt/xerogel-ATO were indistinguishable from the BoL iV performance (Figure 4). Dramatic performance losses were indeed observed for Pt/C even after 1,000 cycles.

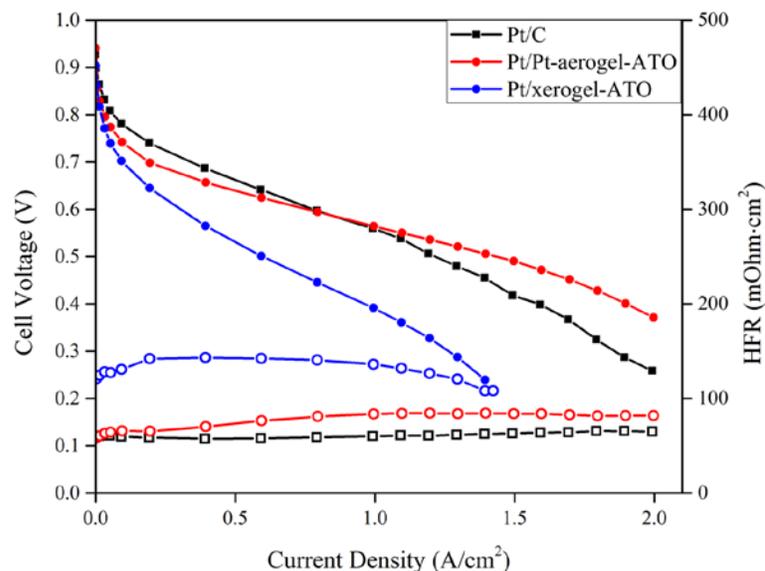


Figure 3. Comparison of fuel cell performance (H₂/air) obtained for Pt/xerogel-ATO, Pt/Pt-aerogel-ATO, and Pt/Vulcan Carbon at 80 °C, 90% relative humidity, and 200 kPa_{abs}. Pt loading at the cathode: 0.10 mg_{Pt}/cm². Pt loading at the anode: 0.10 mg_{Pt}/cm².

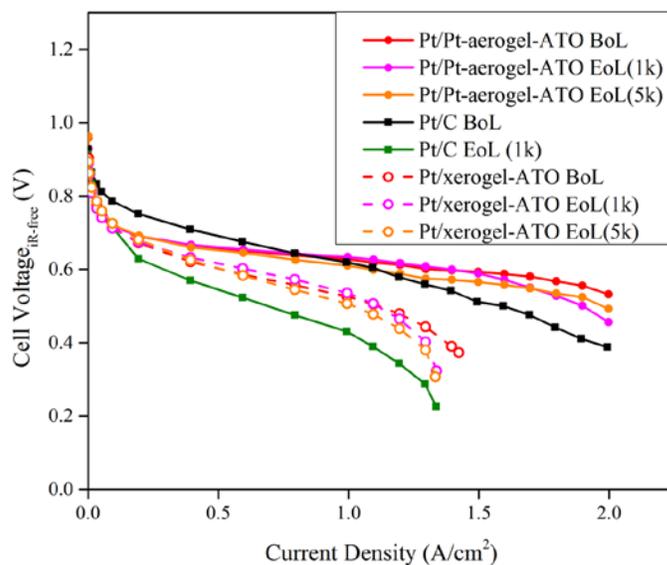


Figure 4. Comparison of fuel cell performance (H_2/air , iR -free) obtained for Pt/xerogel-ATO, Pt/Pt-aerogel-ATO, and Pt/Vulcan Carbon before (BoL) and after (end of life) start-stop protocol for 1,000 and 5,000 cycles at $80^\circ C$, 90% relative humidity, and 200 kPa_{abs} . Pt loading at the cathode: $0.10\text{ mg}_{Pt}/\text{cm}^2$. Pt loading at the anode: $0.10\text{ mg}_{Pt}/\text{cm}^2$.

CONCLUSIONS AND FUTURE DIRECTIONS

We have used DFT to identify different doped oxides that facilitate SMSI and decrease the overpotential for ORR. In parallel, we have synthesized high-surface-area and high-conductivity NTO and successfully deposited Pt on this support yielding higher activity than the Pt/C. The improvement of activity can be ascribed to SMSI, which was confirmed by XPS. ATO was synthesized by the xerogel and Pt-seeded aerogel methods and Pt was deposited using the colloidal method. Both catalysts showed significant stability in the fuel cell accelerated test, and Pt/Pt-aerogel-ATO displayed a better fuel cell performance that was close to that of the commercial Pt/C. For the improvement of BoL performance (to reach the levels of the commercial Pt/C catalysts in terms of iV performance and ORR activity as required by DOE), catalyst and support optimization and/or catalyst layer optimization (catalyst layer thickness, ionomer loadings, and electrode porosity) will be performed. We plan to prepare more homogeneous ATO supports and to deposit Pt using atomic layer deposition (ALD). It is expected that ALD-deposited Pt catalyst would result in better BoL performance and mass activities.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. Cheng He, Shrihari Sankarasubramanian, Vijay K Ramani, "Pt Supported on Nb-Doped-TiO₂ as a Highly Selective and Durable Electrocatalyst for PEFC Applications," Meeting Abstracts, *The Electrochemical Society*.

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2. V. Stamenkovic, B.S. Mun, K.J. Mayrhofer, P.N. Ross, N.M. Markovic, J. Rossmeisl, J. Greeley, and J.K. Nørskov, "Changing the activity of electrocatalysts for oxygen reduction by tuning the surface electronic structure," *Angew. Chem. Int. Ed.* 45 (2006): 2897–2901.